

PCT

WORLD INTELLECTUAL
PROPERTY ORGANIZATION

WO 9604214A1

INTERNATIONAL APPLICATION PUBLISHED I

(51) International Patent Classification ⁶ : C03C 13/06, C04B 35/622		A1	(11) International Publication Number: WO 96/04214 (43) International Publication Date: 15 February 1996 (15.02.96)
(21) International Application Number: PCT/GB95/01797 (22) International Filing Date: 31 July 1995 (31.07.95) (30) Priority Data: 9415586.8 2 August 1994 (02.08.94) GB 9508683.1 28 April 1995 (28.04.95) GB (71) Applicant (for all designated States except US): THE MORGAN CRUCIBLE COMPANY PLC [GB/GB]; Morgan House, Madeira Walk, Windsor, Berkshire SL4 1EP (GB). (72) Inventor; and (75) Inventor/Applicant (for US only): JUBB, Gary, Anthony [GB/GB]; 16 Walton Close, Stourport-on-Severn, Worcestershire DY13 0LS (GB). (74) Agent: PHILLIPS & LEIGH; 7 Staple Inn, Holborn, London WC1V 7QF (GB).		(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG). Published With international search report.	

(54) Title: INORGANIC FIBRES

(57) Abstract

Inorganic fibres are disclosed, vacuum preforms of which have a shrinkage of 3.5 % or less when exposed to 1260 °C for 24 hours. The fibres have a composition comprising SrO, Al₂O₃, and sufficient fibre forming additive to allow fibre formation but not so much as to increase shrinkage beyond 3.5 %. A preferred range of fibres has a shrinkage of 3.5 % or less when exposed to 1500 °C for 24 hours and may comprise (in weight percent): SrO 53.2 %-57.6 %, Al₂O₃ 30.4-40.1 %, SiO₂ 5.06-10.1 %.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

INORGANIC FIBRES

This invention relates to man-made inorganic oxide fibres. The invention also relates to products formed from such fibres.

Inorganic fibrous materials are well known and widely used for many purposes (e.g. as thermal or acoustic insulation in bulk, mat. or blanket form, as vacuum formed shapes, as vacuum formed boards and papers, and as ropes, yarns or textiles; as a reinforcing fibre for building materials; as a constituent of brake blocks for vehicles). In most of these applications the properties for which inorganic fibrous materials are used require resistance to heat, and often resistance to aggressive chemical environments.

Inorganic fibrous materials can be either glassy or crystalline. Asbestos is an inorganic fibrous material one form of which has been strongly implicated in respiratory disease.

It is still not clear what the causative mechanism is that relates some asbestos with disease but some researchers believe that the mechanism is mechanical and size related. Asbestos of a critical size can pierce cells in the body and so, through long and repeated cell injury, have a bad effect on health. Whether this mechanism is true or not regulatory agencies have indicated a desire to categorise any inorganic fibre product that has a respiratory fraction as hazardous, regardless of whether there is any evidence to support such categorisation. Unfortunately for many of the applications for which inorganic fibres are used, there are no realistic substitutes.

Accordingly there is a demand for inorganic fibres that will pose as little risk as possible (if any) and for which there are objective grounds to believe them safe.

One line of study has proposed that if inorganic fibres were made that were sufficiently soluble in physiological fluids that their residence time in the human body was short; then damage would not occur or at least be minimised. As the risk of asbestos linked disease appears to depend very much on the length of exposure this idea appears reasonable. Asbestos is extremely insoluble.

As intercellular fluid is saline in nature the importance of fibre solubility in saline solution has long been recognised. If fibres are soluble in physiological saline solution then, provided the dissolved components are not toxic, the fibres should be safer than fibres which are not so soluble. The shorter the time a fibre is resident in the body the less damage it can do.

Such fibres are exemplified by the applicant's earlier International Patent Applications WO93/15028 and WO94/15883 which disclose saline soluble fibres usable at temperatures of 1000°C and 1260°C respectively

An alternative line of study has proposed that hydratable fibres that lose their fibrous nature in body fluids may offer another route to "safe" fibres in that the shape and size of the fibres may be what is causing damage. This route is exemplified by European Patent Application Nos. 0586797 and 0585547 which are aimed at providing silica free compositions and which disclose two calcium aluminate compositions (one containing 50/50 wt% alumina/calcined lime and the other disclosing 63/30 wt% alumina/calcined lime with additions of 5% CaSO_4 and 2% other oxides). Such fibres hydrate readily so losing their fibrous nature. Asbestos does not hydrate and seems to maintain its fibrous shape in body fluids effectively indefinitely.

The applicants have found that strontium aluminate compositions do not appear to form fibres when blown from a melt whereas such compositions including additives such as silica do form fibres when blown from a melt. Such fibres appear to hydrate in the manner of calcium aluminate fibres and additionally show the potential for high temperature use. Vacuum formed preforms of some such fibres show shrinkages of 3.5% or less when exposed to 1260°C for 24 hours; some show shrinkages of 3.5% or less when exposed to 1400°C for 24 hours; and some even show shrinkages of 3.5% or less when exposed to 1500°C for 24 hours. Such fibres provide a hydratable high temperature fibre usable in the products recited above.

Accordingly the present invention provides an inorganic fibre, a vacuum cast preform of which having a shrinkage of 3.5% or less when exposed to 1260°C for 24 hours, the fibre comprising SrO , Al_2O_3 , and sufficient of a fibre forming additive to allow fibre formation, but not so much as to increase shrinkage beyond 3.5%.

Preferably the fibre forming additive comprises SiO_2 and the constituents SrO , Al_2O_3 , and SiO_2 comprise at least 90wt% (more preferably at least 95wt%) of the fibre composition.

The scope of the invention is made clear in the appended claims with reference to the following description.

In the following, where reference is made to a saline soluble fibre, this is to be taken as meaning a fibre having a total solubility of greater than 10ppm in saline solution as measured by the method described below, and preferably having much higher solubility.

The experimental results are described below with reference to Tables 1, 2, and 3.

Table 1 shows a series of compositions that were melted and blown in a conventional manner. Those compositions indicated as "&" did not form fibre to

a useful extent but formed shot. For each of the compositions the analysed composition in weight percent (found from x-ray fluorescence analysis) is shown. Where a figure "<0.05" is shown this means that the component concerned could not be detected.

Owing to the nature of x-ray fluorescence measurements (which are sensitive to the surrounding environment) the total quantity of material found by analysis can add up to over 100% and in this patent specification (including the description claims and abstract) the figures have not been normalised to 100%. For each composition however the total quantity of analysed material is indicated and it can be seen that the variation from 100% is small. Under the column headed "Relative weight percent" the weight percentage of SrO , Al_2O_3 and SiO_2 to the total of these components is indicated. Except where the context dictates otherwise any percentages quoted in this specification should be taken as percentages as analysed by x-ray fluorescence analysis and not absolute percentages.

Table 2 shows (in the same order as Table 1) shrinkage and solubility data for the fibre forming compositions. Solubility is expressed as parts per million in solution as measured in the method described below.

All of the compositions above and including line A of Tables 1 and 2 include 2.76wt% or less SiO_2 . It can be seen that most of these compositions did not form fibre. Some of the fibres include Na_2O in amounts of 2.46wt% or more to assist fibre forming but show poor shrinkage characteristics at temperatures above 1000°C (in the sense of more than 3.5% at measured temperature).

One fibre (SA5(2.5%K₂O/SiO₂)) which contains 1.96% K_2O and 2.69% SiO_2 has acceptable shrinkage at 1260°C.

Thus it can be seen that "pure" strontium aluminates do not form fibres whereas by addition of fibre forming additives (e.g. SiO_2 and Na_2O) fibres may be formed. The shrinkage characteristics of the resultant fibres depend upon the additives used.

The fibres below line A and above and including line B have a SrO content of less than 35wt% and show poor shrinkage characteristics. The fibres shown below line B have a SrO content of greater than 35wt% and where measured show acceptable shrinkage at 1260°C.

The fibre of line C comprises 2.52wt% CaO and this appears to be damaging to performance at 1400°C. The fibres lying below line D and above and including line E have an Al_2O_3 content of greater than 48.8wt% which appears to affect adversely the performance of the fibres at 1400°C. The fibre

below line E has a SiO_2 content of 14.9wt% which appears to be bad for 1400°C performance (see below for 1500°C performance).

A further limited range of compositions (shown as bold text under the column 1400°C) tend to have an acceptable shrinkage at 1400°C. These compositions lie below line C and above and including line D of Tables 1 & 2. The two fibres indicated in this range that do not meet the 3.5% shrinkage requirement may just be anomalous results.

The fibres lying below line C and above and including line D have been sorted on relative weight percent SrO (as defined above) and it can be seen that those compositions with a relative weight percent SrO of greater than 53.7% and less than 59.6% tend to have acceptable shrinkages at 1500°C. The fibre in this region that does not have acceptable shrinkage at 1500°C is a high SiO_2 fibre (12.2wt% SiO_2) and this supports the deleterious effect of too much SiO_2 mentioned above.

Two fibres (SA5a and SA5aII) show acceptable shrinkage at 1550°C.

Additionally it can be seen that some of the fibres show enormous solubilities and so may provide usable refractory fibres that will dissolve in body fluids.

All of the fibres showed hydration on insertion into aqueous fluids, indeed they tended to show some hydration on forming the preforms that were used for shrinkage testing. After 24 hour solubility testing in physiological-type fluids the hydration is very evident. The hydration takes the form of apparent dissolution and re-precipitation of crystals on the fibre surface that results in it losing its fibrous nature.

For some of the compositions, in making the vacuum preforms for testing, a dispersant and wetting agent was used (Troy EX 516-2 (Trade mark of Troy Chemical Corporation)) which is a mixture of non-ionic surfactants and chemically modified fatty acids. This was in an attempt to minimise the time of exposure to water and hence the extent of hydration. It can be seen from Table 3 (which shows the same type of information as Table 2) that those compositions where the dispersant was used (indicated as "troy") tend to have a higher shrinkage than the identical composition not using the dispersant. The applicants surmise that this may be due to the partial hydration "locking" the fibres together so that any one fibre has to shrink against the tension of supporting fibres along its length: such tension may lead to fibre thinning rather than longitudinal shrinkage. When the dispersant is used the fibres are free to shrink along their length.

The following describes in detail the methods used to measure shrinkage and solubility.

Shrinkage was measured by proposed ISO standard ISO/TC33/SC2/N220 (equivalent to British Standard BS 1920, part 6:1986) with some modifications to account for small sample size. The method in summary comprises the manufacture of vacuum cast preforms, using 75g of fibre in 500cm³ of 0.2% starch solution, into a 120 x 65mm tool. Platinum pins (approximately 0.5mm diameter) were placed 100 x 45mm apart in the 4 corners. The longest lengths (L1 & L2) and the diagonals (L3 & L4) were measured to an accuracy of $\pm 5\mu\text{m}$ using a travelling microscope. The samples were placed in a furnace and ramped to a temperature 50°C below the test temperature at 300°C/hour and ramped at 120°C/hour for the last 50°C to test temperature and left for 24 hours. The shrinkage values are given as an average of the 4 measurements.

It should be noted that although this is a standard way of measuring shrinkage of fibre it has an inherent variability in that the finished density of the preform may vary depending on casting conditions. Further it should be noted that fibre blanket will usually have a higher shrinkage than a preform made of the same fibre. Accordingly the 3.5% figure mentioned in this specification is likely to translate as a higher shrinkage in finished blanket.

Solubility was measured by the following method.

The fibre was first chopped through a 10 mesh sieve and shot removed by hand sieving also through a 10 mesh sieve.

The solubility test apparatus comprised a shaking incubator water bath, and the test solution had the following composition:-

<u>Compound</u>	<u>Name</u>	<u>Grams</u>
NaCl	Sodium chloride	6.780
NH ₄ Cl	Ammonium chloride	0.540
NaHCO ₃	Sodium bicarbonate	2.270
Na ₂ HPO ₄ ·H ₂ O	Disodium hydrogen phosphate	0.170
Na ₃ C ₆ H ₅ O ₇ ·2H ₂ O	Sodium citrate dihydrate	0.060
H ₂ NCH ₂ CO ₂ H	Glycine	0.450
H ₂ SO ₄ s.g. 1.84	Sulphuric acid	0.050

The above materials were diluted to 1 litre with distilled water to form a physiological-like saline solution.

0.500 grams = 0.003 grams of chopped fibre was weighed into a plastic centrifuge tube and 25 cm³ of the above saline solution added. The fibre and saline solution was shaken well and inserted into the shaking incubator water bath maintained at body temperature (37°C = 1°C). The shaker speed was set at 20 cycles/minute.

After 24 hours the centrifuge tube was removed then supernatant liquid was decanted and the liquid passed through a filter (0.45 micron cellulose nitrate membrane filter paper [WCN type from Whatman Labsales Limited]) into a clean plastic bottle. The liquid was then analysed by one of two methods. The first method used was atomic absorption using a Thermo Jarrell Ash Smith - Hieffe II machine.

The operating conditions were as set out in the applicant's earlier earlier International Patent Applications WO93/15028 and WO94/15883. For SrO the operating conditions were:-

WAVELENGTH <u>(nm)</u>	BAND <u>WIDTH</u>	CURRENT <u>(mA)</u>	<u>FLAME</u>
460.7	0	12	Fuel Lean

Strontium is measured against a standard atomic absorption solution (Aldrich 970µm/ml). Three standards are prepared to which 0.1%KCl is added (Sr [ppm] 9.7,3.9 & 1.9). Dilutions of x10 and x20 are normally made to measure Sr level in the sample. SrO is then calculated as 1.183xSr.

All stock solutions were stored in plastic bottles.

In the second method used (which was shown to give results consistent with the first method) element concentrations were found by inductively coupled plasma - atomic emission spectroscopy in known manner.

The above has discussed resistance to shrinkage of preforms exposed to 1260°C for 24 hours. This is an indication of the maximum use temperature of a fibre. In practice fibres are quoted for a maximum continuous use temperature and a higher maximum exposure temperature. It is usual in industry when selecting a fibre for use at a given temperature to choose a fibre having a higher continuous use temperature than that nominally required for the intended use. This is so that any accidental increase in temperature does not damage the fibres. It is quite usual for a margin of 100 to 150°C to be given.

The applicants are not certain as yet as to how much other oxides or other impurities will affect the performance of fibres as described above and the appendant claims allow, where SiO_2 is the fibre forming additive, up to 10wt% of materials other than SrO , Al_2O_3 and SiO_2 , although this should not be seen as limitative.

Although the above description has referred to manufacture of fibres by blowing from a melt the invention is not limited to blowing and also encompasses spinning and other techniques in which fibres are formed from a melt, and also encompasses fibres made by any other process.

Table 1 - Part 1

Comp.	Composition wt%											Relative weight percent (to total SrO+Al2O3+SiO2)				
	SrO	Al2O3	SiO2	CaO	MgO	ZrO2	BaO	K2O	Na2O	P2O5	Fe2O3	Cr2O3	Total	SrO	Al2O3	SiO2
& SA3 & SA1 & SA2	33.1	60.9	<0.05	0.08	<0.05	<0.05	0.20	<0.05	<0.05	0.06	1.92	<0.05	94.34	35.2%	64.8%	
	61.4	37.1	<0.05	0.08	<0.05	<0.05	0.30	<0.05	<0.05	<0.05	<0.05	<0.05	98.58	62.3%	37.7%	
	48.5	49.7	<0.05	0.06	<0.05	<0.05	0.24	<0.05	<0.05	<0.05	0.64	<0.05	98.50	49.4%	50.6%	
SA5(5%Na2O) SA5(2.5%Na2O) & SA5c & SA8c & SA3c	54.8	39.3	0.14	0.08	<0.05	<0.05	0.21	<0.05	5.14	<0.05	<0.05	<0.05	99.67	58.1%	41.7%	0.1%
	54.5	41.2	0.19	0.31	<0.05	<0.05	0.21	<0.05	2.46	<0.05	<0.05	<0.05	98.87	56.8%	43.0%	0.2%
	50	39.4	2.51	0.08	3.29	<0.05	0.21	<0.05	<0.05	<0.05	1.07	<0.05	98.56	54.4%	42.9%	2.7%
SA5(2.5%Na2O/SiO2) SA5(2.5%K2O/SiO2) & SA4c & SA2c	24.1	72.9	2.52	0.06	<0.05	<0.05	0.10	<0.05	0.12	<0.05	<0.05	<0.05	99.80	24.2%	73.3%	2.5%
	39.9	55.4	2.55	0.07	0.12	<0.05	0.19	<0.05	<0.05	<0.05	<0.05	<0.05	98.31	40.8%	56.6%	2.6%
	56.4	38.8	2.57	0.20	0.08	<0.05	0.21	<0.05	2.57	<0.05	<0.05	<0.05	100.83	57.7%	39.7%	2.6%
SA5(2.5%K2O/SiO2) SA9c & SA4c & SA2c	56.3	38.8	2.69	0.13	<0.05	<0.05	0.21	1.86	0.15	<0.05	0.36	<0.05	100.50	57.6%	39.7%	2.8%
	44.5	52	2.71	0.07	<0.05	<0.05	0.17	<0.05	<0.05	<0.05	0.05	<0.05	99.50	44.9%	52.4%	2.7%
	54.5	37.3	2.74	0.30	0.16	0.54	0.66	<0.05	0.22	<0.05	0.08	<0.05	96.50	57.6%	39.5%	2.9%
SA8b SA7b SA7a SA6b SA6d SA6a SACS1	48.1	47.1	2.76	0.08	<0.05	<0.05	0.22	<0.05	<0.05	<0.05	0.08	<0.05	98.34	49.1%	48.1%	2.8%
	22.9	65.7	9.62	0.06	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.06	<0.05	98.28	23.3%	66.9%	9.8%
	26.2	62.4	9.62	0.10	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.08	<0.05	98.32	26.7%	63.5%	9.8%
	27.4	62.2	9.20	0.06	<0.05	0.06	0.16	<0.05	<0.05	<0.05	0.10	<0.05	99.18	27.7%	63.0%	9.3%
	32.9	56.1	9.43	0.06	<0.05	<0.05	0.16	<0.05	<0.05	<0.05	0.18	<0.05	98.65	33.4%	57.0%	9.6%
	32.9	58.8	7.09	0.07	<0.05	<0.05	0.11	<0.05	0.10	<0.05	<0.05	<0.05	99.07	33.3%	59.5%	7.2%
	33.6	59.5	5.12	0.08	0.14	<0.05	0.20	<0.05	<0.05	<0.05	<0.05	<0.05	98.64	34.2%	60.6%	5.2%
	53.9	37.8	5.25	2.52	0.18	<0.05	0.23	<0.05	0.13	<0.05	<0.05	<0.05	100.01	55.6%	39.0%	5.4%

Table 1 - Part 2

Comp.	Composition wt%											Relative weight percent (to total SrO+Al2O3+SiO2)				
	SrO	Al2O3	SiO2	CaO	MgO	ZrO2	BaO	K2O	Na2O	P2O5	Fe2O3	Cr2O3	Total	SrO	Al2O3	SiO2
SAR8	44.7	47.4	7.65	0.07	0.10	<0.05	0.19	<0.05	0.10	<0.05	<0.05	<0.05	100.20	44.8%	47.5%	7.7%
SAR5	45	44.9	9.77	0.06	<0.05	<0.05	0.17	<0.05	0.09	<0.05	<0.05	<0.05	100.00	45.1%	45.0%	9.8%
SAR9	47.5	45.4	5.30	0.24	0.11	<0.05	0.20	<0.05	0.19	<0.05	0.05	<0.05	99.00	48.4%	46.2%	5.4%
SA2a	48.9	44.8	4.72	0.08	<0.05	<0.05	0.24	<0.05	<0.05	<0.05	0.32	<0.05	99.06	49.7%	45.5%	4.8%
SAR4	50.5	39.8	9.85	0.07	<0.05	<0.05	0.18	<0.05	0.10	<0.05	<0.05	<0.05	100.50	50.4%	39.7%	9.8%
SAR7	50.8	42.3	7.41	0.07	0.05	<0.05	0.18	<0.05	0.13	<0.05	<0.05	<0.05	100.90	50.5%	42.1%	7.4%
SAR1	52.2	35.7	12.00	0.09	0.05	0.15	0.20	<0.05	0.12	<0.05	0.05	<0.05	100.60	52.3%	35.7%	12.0%
SA5d	53	39	7.63	0.10	0.12	<0.05	0.22	<0.05	0.23	<0.05	<0.05	<0.05	100.30	53.2%	39.1%	7.7%
SA5d II	54.2	39.6	7.57	0.08	0.08	<0.05	0.20	<0.05	0.23	<0.05	0.07	<0.05	101.96	53.5%	39.1%	7.5%
SA5b	52.3	35.1	10.00	0.10	0.12	<0.05	0.24	<0.05	<0.05	<0.05	<0.05	<0.05	97.86	53.7%	36.0%	10.3%
SA5a	53.2	39.9	5.34	0.14	<0.05	<0.05	0.26	<0.05	<0.05	<0.05	<0.05	<0.05	98.84	54.0%	40.5%	5.4%
SA5a II	54.9	40.1	5.06	0.08	<0.05	<0.05	0.26	<0.05	<0.05	<0.05	<0.05	<0.05	100.89	54.9%	40.1%	5.1%
SAR10	56.4	37.3	6.01	0.14	0.10	<0.05	0.21	<0.05	0.19	<0.05	0.07	<0.05	100.40	56.6%	37.4%	6.0%
SA4d	56.7	34.1	7.37	0.12	0.08	<0.05	0.22	<0.05	0.16	<0.05	0.06	<0.05	98.75	57.8%	34.7%	7.5%
SAR12	57.4	29.2	12.20	0.09	0.09	<0.05	0.23	<0.05	0.19	<0.05	<0.05	<0.05	99.40	58.1%	29.6%	12.3%
SA4b	57.6	30.4	10.10	0.08	<0.05	<0.05	0.30	<0.05	<0.05	<0.05	<0.05	<0.05	96.48	58.7%	31.0%	10.3%
SA4a	58.6	34.4	5.35	0.10	<0.05	<0.05	0.20	<0.05	<0.05	<0.05	0.18	<0.05	98.83	59.6%	35.0%	5.4%
SAR3	61.3	29.9	9.73	0.09	<0.05	<0.05	0.23	<0.05	0.10	<0.05	<0.05	<0.05	101.40	60.7%	29.6%	9.6%
SAR6	61.7	32.4	7.44	0.08	<0.05	<0.05	0.22	<0.05	0.11	<0.05	<0.05	<0.05	102.00	60.8%	31.9%	7.3%
SA1a	63.8	29.9	4.84	0.08	<0.05	<0.05	0.30	<0.05	<0.05	0.08	0.18	0.06	99.22	64.7%	30.3%	4.9%
SA9a	44	48.9	4.95	0.07	<0.05	<0.05	0.21	<0.05	<0.05	<0.05	<0.05	<0.05	98.13	45.0%	50.0%	5.1%
SA3a	41.2	53.1	4.74	0.06	<0.05	<0.05	0.22	<0.05	<0.05	<0.05	0.06	<0.05	99.38	41.6%	53.6%	4.8%
SAR2	54.9	30.6	14.90	0.08	0.05	0.08	0.19	<0.05	0.10	<0.05	<0.05	<0.05	100.90	54.7%	30.5%	14.8%

Table 2 - Part 1

Comp.	Shrinkage at 24 hours (°C)										Relative weight percent (to total SrO+Al2O3+SiO2)			Solubility ppm		
	1000	1200	1260	1350	1400	1450	1500	1550	1600	SrO	Al2O3	SiO2	SrO	Al2O3	SiO2, Total	
SA3 &										35.2%	64.8%					
SA1 &										62.3%	37.7%					
SA2 &										49.4%	50.6%					
SA5(5%Na2O)										58.1%	41.7%	0.1%	65	1000	1 1066	
SA5(2.5%Na2O)					8.22					56.8%	43.0%	0.2%	1	563	1 565	
SA5c &		3.38	8.64							54.4%	42.9%	2.7%				
SA8c &										24.2%	73.3%	2.5%				
SA3c &										40.8%	56.6%	2.6%				
SA5(2.5%Na2O/SiO2)		2.39	6.53							57.7%	39.7%	2.6%	10	500	1 511	
SA5(2.5%K2O/SiO2)		3.95	3.02							57.6%	39.7%	2.8%	11		2 13	
SA9c &										44.9%	52.4%	2.7%				
SA4c &										57.6%	39.5%	2.9%				
SA2C &										49.1%	48.1%	2.8%			A	
SA8b	10.16		12.1							23.3%	66.9%	9.8%	5	2	3 10	
SA7b	4.82		5.33							26.7%	63.5%	9.8%				
SA7a	4.4		5.4		9.94					27.7%	63.0%	9.3%	4	2	2 8	
SA6b	3.62		6.42							33.4%	57.0%	9.6%	5	1	1 7	
SA6d			7.48		7.8					33.3%	59.5%	7.2%	4	1	1 6	
SA6a	7.02		8.81		6.52					34.2%	60.6%	5.2%	8	2	3 13	
SACS1			2.15		4.8					55.6%	39.0%	5.4%	26	1	2 29	

A

B

C

Table 2 - Part 2

Comp.	Shrinkage at 24 hours (°C)										Relative weight percent (to total SrO+Al ₂ O ₃ +SiO ₂)				Solubility ppm			
	1000	1200	1260	1350	1400	1450	1500	1550	1600		SrO	Al ₂ O ₃	SiO ₂	Total	SrO	Al ₂ O ₃	SiO ₂	Total
SAR8		0.94			1.14	7.86	39.6				44.8%	47.5%	7.7%	6	6			6
SAR5		1.55			1.61	1.70	33.6				45.1%	45.0%	9.8%	11	8	2	1	11
SAR9		1.25	2.85	3.77	5.91						48.4%	46.2%	5.4%	20	10		10	20
SA2a			1.61		2.67	7.75					49.7%	45.5%	4.8%	17	10	1	6	17
SAR4		1.06			1.6	3.19	31.1				50.4%	39.7%	9.8%	6	6			6
SAR7		1.07		2.26	2.94	4.7					50.5%	42.1%	7.4%	7	7			7
SAR1	0.75	1.10	1.19	1.36	2.14	25.25					52.3%	35.7%	12.0%	15	14	1	1	15
SA5d					1.36		4.21				53.2%	39.1%	7.7%	19	17	1	1	19
SA5d II					1.3		4.13				53.5%	39.1%	7.5%					
SA5b	0.6		0.69		0.66	2.6	4.7				53.7%	36.0%	10.3%	14	11		3	14
SA5a			0.89		1.1		1.78				54.0%	40.5%	5.4%	47	45		2	47
SA5a II					2.71	2.75	2.86	3.14	5.88		54.9%	40.1%	5.1%					
SAR10	2.18	2.2	2.23		2.48	2.77	2.51	Melts	6.9		56.6%	37.4%	6.0%	63	56		7	63
SA4d					1.69	2.77	3.36				57.8%	34.7%	7.5%	18	15	1	2	18
SAR12		1.4	1.4		1.31		Melts				58.1%	29.6%	12.3%	27	25		2	27
SA4b	0.55		0.41		1.19	1.16	1.93	7.9			58.7%	31.0%	10.3%	18	15		3	18
SA4a			1.56		4.6						59.6%	35.0%	5.4%	22	19	1	2	22
SAR3		1.49	1.35	1.98	2.21	5.31					60.7%	29.6%	9.6%	24	22		2	24
SAR6		1.42			2.22	2.42	6.36	8.19			60.8%	31.9%	7.3%	15	15		2	15
SA1a			2.37		8.57						64.7%	30.3%	4.9%	1062	161	897	4	1062
SA9a					7.19						45.0%	50.0%	5.1%	7	5	1	1	7
SA3a	1.12		2.45	3.94	6.43						41.6%	53.6%	4.8%	21	12	3	6	21
SAR2		0.73	2.00	3.94	8.43						54.7%	30.5%	14.8%	16	14		2	16

Table 3

Comp.	Shrinkage at 24 hours (°C)										Relative weight percent (to total SiO ₂ +Al ₂ O ₃ +SiO ₂)				Solubility			
	1000	1200	1260	1350	1400	1450	1500	1550	1600		SiO ₂	Al ₂ O ₃	SiO ₂	SiO ₂	SiO	Al ₂ O ₃	SiO ₂	Total
SA4d					1.69	2.77	3.36		6.9		57.8%	34.7%	7.5%		13	1	1	15
SA4d (tray)					3.12	3.86	4.72		13.62		57.8%	34.7%	7.5%					
SA5a II					2.71	2.75	2.86	3.14			54.9%	40.1%	5.1%					
SA5a II-tray					1.56				14.2		54.9%	40.1%	5.1%					
SA5d					1.36		4.21				53.2%	39.1%	7.7%		17	1	1	19
SA5d (tray)					0.93		6.04				53.2%	39.1%	7.7%					
SA5d II					1.3		4.13				53.5%	39.1%	7.5%					
SA5d II (tray)					1.35		5.21				53.5%	39.1%	7.5%					
SA5(2.5%Na ₂ O/SiO ₂)	2.39	3.95	6.53								57.7%	39.7%	2.6%					
SA5(2.5%Na ₂ O/SiO ₂) tray			7.17								57.7%	39.7%	2.6%					
SA5(5%Na ₂ O)						8.22					58.1%	41.7%	0.1%		50	1200	1	1251
SA5(5%Na ₂ O) tray						14.47					58.1%	41.7%	0.1%					
SA6b	3.62		6.42								33.4%	57.0%	9.6%		7	2	2	11
SA6b (tray)			13.18								33.4%	57.0%	9.6%					

Claims

1. An inorganic fibre, a vacuum preform of which has a shrinkage of 3.5% or less when exposed to 1260°C for 24 hours, the fibre having a composition comprising SrO, Al_2O_3 , and sufficient fibre forming additive to allow fibre formation but not so much as to increase shrinkage beyond 3.5%.
2. An inorganic fibre as claimed in claim 1, in which the fibre forming additive comprises SiO_2 and the constituents SrO, Al_2O_3 , and SiO_2 comprise at least 90wt% of the fibre composition.
3. An inorganic fibre as claimed in claim 2 in which the constituents SrO, Al_2O_3 , and SiO_2 comprise at least 95wt% of the fibre composition.
4. An inorganic fibre as claimed in any preceding claim and comprising 35wt% or more SrO
5. An inorganic fibre as claimed in any preceding claim and comprising
SrO 41.2wt% - 63.8wt%
 Al_2O_3 29.9wt% - 53.1wt%
6. An inorganic fibre as claimed in claim 5 and comprising greater than 2.76wt% to less than 14.9wt% SiO_2 .
7. An inorganic fibre as claimed in any preceding claim, a vacuum preform of which has a shrinkage of 3.5% or less when exposed to 1400°C for 24 hours.
8. An inorganic fibre as claimed in claim 7 in which the amount of Al_2O_3 is 48.8wt% or less.

9. An inorganic fibre as claimed in any preceding claim, a vacuum preform of which has a shrinkage of 3.5% or less when exposed to 1500°C for 24 hours.
10. An inorganic fibre as claimed in claim 9 in which the weight percentage of SrO relative to the total amount of SrO plus Al_2O_3 plus SiO_2 is in the range greater than 53.7wt% to less than 59.6wt %.
11. An inorganic fibre as claimed in claim 10 and comprising in wt%:-
- | | |
|-------------------------|-----------------|
| SrO | 53.2wt%-57.6wt% |
| Al_2O_3 | 30.4wt%-40.1wt% |
| SiO_2 | 5.06wt%-10.1wt% |
12. An inorganic fibre as claimed in any preceding claim comprising Na_2O in an amount less than 2.46wt%.
13. An inorganic fibre as claimed in any preceding claim, a vacuum preform of which has a shrinkage of 3.5% or less when exposed to 1550°C for 24 hours.
14. An inorganic fibre as claimed in claim 13 and comprising:-
- | | |
|-------------------------|-----------------|
| SrO | 53.2wt%-54.9wt% |
| Al_2O_3 | 39.9wt%-40.1wt% |
| SiO_2 | 5.06wt%-5.34wt% |
15. A saline soluble inorganic fibre as claimed in any preceding claim.
16. A hydratable saline soluble inorganic fibre as claimed in any preceding claim.
17. A hydratable saline soluble inorganic fibre having a shrinkage of 3.5% or less when exposed to 1260°C for 24 hours

18. A hydratable saline soluble inorganic fibre having a shrinkage of 3.5% or less when exposed to 1400°C for 24 hours.
19. A hydratable saline soluble inorganic fibre having a shrinkage of 3.5% or less when exposed to 1500°C for 24 hours.
20. A process for the formation of fibres from a melt comprising predominantly SrO and Al_2O_3 in which minor amounts of SiO_2 are added to allow fibre formation.

INTERNATIONAL SEARCH REPORT

Int. Application No.
PCT/GB 95/01797

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C03C13/06 C04B35/622

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C03C C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 7814 Derwent Publications Ltd., London, GB; Class F01, AN 78-25915A & JP,A,52 139 113 (ASAHI GLASS KK) , 19 November 1977 see abstract ---	1-20
A	EP,A,0 586 797 (DIDIER-WERKE AG) 16 March 1994 cited in the application see abstract -----	1-20

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search

30 October 1995

Date of mailing of the international search report

27. 11. 95

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+ 31-70) 340-3016

Authorized officer

Van Bomme1, L

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 95/01797

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-586797	16-03-94	DE-C- 4228353	28-04-94
		AU-B- 4490993	03-03-94
		JP-A- 6272116	27-09-94
		US-A- 5346868	13-09-94
